ELECTROCHEMICAL SENSOR FOR SCALE BUILDING UP MEASUREMENTS


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2

3    The present invention relates to an electrochemical

4    sensor apparatus and method and, in particular to an

5    electrochemical sensor that can be used to measure scale,

6    such as mineral scale or other particulates, which

7    deposit on the surface of pipelines or process equipment.

8

9    Mineral scale formation is one of the major flow

10   assurance concerns in the chemical industry.  The problem

11   of scale build up arises where a fluid is flowing through

12   a pipe or vessel and particulates precipitate out from

13   the fluid and deposit on the surfaces of fluid-carrying

14   equipment.  This can cause a blockage to form and to the

15   eventual failure of the equipment or disruption in the

16   flow of the fluid.

17

18   This problem is particularly apparent in the offshore oil

19   and gas industry. If the formation of scale or other

20   particulate masses goes uncontrolled, the operational

21   safety of the process or plant equipment can be

22   compromised through the failure of subsea safety and flow

23   control valves or other process equipment. If, for

1   example, a large mass of mineral scale forms in the riser

2   from an oil well, the mass of scale will cause the riser

3   to be blocked, consequently the flow of oil well fluids

4   will be impeded and the pressure will greatly increase,

5   thereby causing the riser to break.

6

7   In view of this problem, it is desirable to be able to

8   measure the amount of scale that has formed within a

9   conduit or vessel, and also to be able to estimate and

10  monitor the changes of likelihood that a fluid will

11  precipitate out scale or other particulates. A

12  measurement of the surface deposition on control surfaces

13  or changes of scaling tendency will alert the operator to

14  a build-up of scale. Hence, the operator of the well or

15  chemical process will be able to treat the fluid in order

16  to prevent scaling.

17

18  Current methods for monitoring the extent of surface

19  scaling and the scaling tendency in reservoirs or pipes

20  have limitations.  They tend to involve measuring water

21  or other fluid samples, or to involve the measurement of

22  flow variables such as pressure.  These methods do not

23  allow the operator to predict whether scaling will occur.

24  Scale detection often comes too late using this type of

25  monitoring, typically after a decrease in production. In

26  general, efforts to control the scaling problem have

27  concentrated upon strategies to mechanically or

28  chemically remove scale.

29

30  It is an object of the present invention to develop an

31  electrochemical sensor that allows the operator to

32  measure the extent of scale formation on a surface and to

33  assess the scaling tendency of a fluid.

1

2   In accordance with a first aspect of the present

3   invention, there is provided an electrochemical sensor

4   comprising:

5   an electrochemical cell having a sensor means;

6   fluid flow control means positioned so as to release a

7   fluid jet onto the sensor means, the fluid flow control

8   means having means for controlling the velocity of the

9   fluid jet, the fluid flow velocity being defined by the

10   Reynolds number of the fluid when the fluid is in the

11   fluid flow control means; and

12   wherein control of the Reynolds number and measurement of

13   the electrical output of the sensor provide a measure of

14   the build-up of scale on the working electrode.

15

16   Preferably, the measure of scale build up quantifies the

17   scale build up on the sensor surface in the

18   electrochemical cell.

19

20   Preferably, the sensor detects scale build up to measure

21   the scaling tendency of the fluid.

22

23   Preferably, the fluid control means is a conduit provided

24   with a control valve or pump.

25

26   Preferably, the sensor measures the change in electrical

27   output as a function of Reynolds Number during use of the

28   fluid flow control means

29

30   Preferably, the electrical output measurement means

31   measures the limiting current response of the sensor as a

32   function of Reynolds Number.

33

4

1    Preferably, the fluid flow control means is a conduit

2    having a predefined diameter (d) and is positioned at a

3    height (H) above the sensor having a radius (r).

4

5    Preferably, laminar flow of the fluid from the fluid

6    control means is provided by setting said diameter (d),

7    height (H) and radius (r).

8

9    Preferably, $H/d = 1$; and $r/d < 0.5$.

10

11   Preferably, the apparatus of the present invention

12   further comprises fluid sampling means for obtaining a

13   sample of a test fluid.

14

15   Preferably, the fluid sampling means contains fluid

16   isolation means for isolating the test fluid from a bulk

17   fluid.

18

19   Preferably, the test fluid isolation means is provided by

20   a container having at least one sealable valve which,

21   when opened, allows the test fluid to enter the sampling

22   means.

23

24   Preferably, the fluid flow control means comprises a flow

25   meter or flow sensor for measuring flow, connected to a

26   conduit from which said fluid jet is expelled.

27

28   Preferably, the sensor comprises a working electrode, a

29   counting electrode and a reference electrode.

30

31   Preferably, the electrochemical sensor further comprises

32   a reservoir for storing a second, pre-prepared

33   electrolyte, flow control means and one or more conduits

1   connected to the electrical cell such that the pre-

2   prepared electrolyte is used with the electrical cell to

3   measure the quantity of scale deposited by the test fluid

4   by measuring the electrical output of the cell as a

5   function of Reynolds Number.

6

7   In some examples of the present invention it has been

8   found that quantitative measurement of the extent of

9   scaling is more accurately determined by replacing the

10   test fluid with said pre prepared electrolyte in order to

11   make measurements.

12

13   Preferably, the electrolyte is a solution.

14

15   Preferably, the electrolyte is a solution of brine

16   containing a suitable tracer.

17

18   Preferably, the tracer is oxygen.

19

20   Optionally, the tracer is an ion tracer.

21

22   Optionally, the tracer is $Fe(CN)_6^{4-}$.

23

24   Preferably, the pre-prepared solution has a saturation

25   ratio of less than 1.

26

27   Optionally, the pre-prepared solution has a saturation

28   ratio of greater than 1.

29

30   In accordance with a second aspect of the present

31   invention, there is provided a method of measuring the

32   scaling properties of a test fluid, the method comprising

33   the steps of:

1    controlling the velocity of a fluid jet as defined by the
2    Reynolds number of the fluid when the fluid is in a fluid
3    flow control means;
4    releasing the fluid jet from the fluid control means onto
5    a sensor of an electrochemical cell; and
6    measuring the electrical output from the sensor as a
7    function of the Reynolds number of the jet fluid, the
8    sensor being in contact with a sample of the test fluid.
9
10   Preferably, the sensor gives a measure of the change in
11   electrical output as a function of Reynolds number during
12   use of the fluid flow control means.
13
14   Preferably, the electrical output provides a measure of
15   the limiting current response of the electrochemical cell
16   as a function of Reynolds Number.
17
18   Preferably, the fluid flow control means is a conduit
19   having a predefined diameter (d) and is positioned at a
20   height (H) above the working electrode or sensor having a
21   radius (r).
22
23   Preferably, laminar flow of the fluid from the fluid
24   control means is provided by setting said diameter (d),
25   height (H) and radius (r).
26
27   Preferably, H/d = 1; and r/d<0.5.
28
29   Preferably, the test fluid has a saturation ratio of
30   greater than 1.
31   Preferably, the pre-prepared electrolyte is a conductive
32   Brine solution containing an oxygen tracer.
33

1   Optionally, the method comprises the further step of
2   isolating the test fluid from a flowing fluid prior to
3   measuring the electrical output from the electrical cell
4   as a function of the Reynolds number of the fluid.
5
6   Preferably, the test fluid is isolated by closing valves
7   arranged upstream and downstream of a predetermined
8   measuring location in a sample measuring means.
9
10  It has been found that isolation of a sample of the fluid
11  allows the fluid velocity as defined ny the Reynolds
12  Number to be carefully controlled in the sensor device.
13
14  Preferably the fluid is isolated by removably attaching a
15  sampling conduit to a first conduit in which the bulk of
16  the fluid is situated, and by providing valves to isolate
17  the sampling conduit from the first conduit.
18
19  In accordance with a third aspect of the present
20  invention there is provided a method of measuring the
21  scaling properties of a test fluid, the method comprising
22  the steps of:
23  introducing a jet of test fluid into an electrochemical
24  cell so as to allow scale to build up on one or more
25  surfaces in the cell;
26  removing the test fluid from the electrochemical cell;
27  introducing a pre-prepared solution into the cell; and
28  measuring the electrical output from the electrochemical
29  cell.
30
31  Preferably, the test fluid is introduced into the
32  electrochemical cell at a rate defined by the Reynolds

1  Number of the fluid when contained in a first fluid

2  control means.

3

4  Preferably, the pre-prepared solution is introduced into

5  the electrochemical cell at a rate defined by the

6  Reynolds Number of the fluid when contained in a second

7  fluid control means.

8

9  Preferably, the electrical output measures the change in

10  electrical output as a function of Reynolds Number during

11  use of the fluid flow control means.

12

13  Preferably, the electrical output provides a measure of

14  the limiting current response of the electrochemical cell

15  as a function of Reynolds Number.

16

17  Preferably, the fluid flow control means is a conduit

18  having a predefined diameter (d) and is positioned at a

19  height (H) above the working electrode or sensor having a

20  radius (r).

21

22  Preferably, laminar flow of the fluid from the fluid

23  control means is provided by setting said diameter (d),

24  height (H) and radius (r).

25

26  Preferably, $H/d = 1$; and $r/d < 0.5$.

27

28  Preferably, the pre-prepared solution has a saturation

29  ratio of less than 1.

30

31  Optionally, the pre-prepared solution has a saturation

32  ratio of greater than 1.

33

1    In accordance with a fourth aspect of the present

2    invention, there is provided a computer program for use

3    with apparatus of the first aspect of the present

4    invention, and with the method of the second aspect of

5    the present invention, in which analysis of the

6    electrical output and the Reynolds number provides

7    information on the quantity of scale build up and/or the

8    scaling tendency of the fluid.

9

10   The present invention will now be described by way of

11   example only, with reference to the accompanying

12   drawings, in which:

13

14   Figure 1 is a schematic diagram of an embodiment of the

15   apparatus of the present invention;

16

17   Figure 2 is a graph of the limiting current output of the

18   electrochemical cell, as measured against the square root

19   of the Reynolds Number of the jet fluid;

20

21   Figure 3a is a graph of limiting current v Reynolds

22   number which shows it's variation after scaling has

23   occurred, figures 3b and 3c illustrate physical changes

24   to the sensor before and after scaling;

25

26   Figure 4 shows the relationship between the nozzle 12

27   from which the impinging jet emanates and the sensor 22

28

29   Figure 5 is a schematic representation of the second

30   embodiment of the present invention, where the

31   electrochemical cell is positioned in a conduit,

32   removably connected to a riser;

33

1  Figure 6 shows the limiting current correlation with

2  scaling index of the water;

3

4  Figure 7 is a schematic diagram of a third embodiment of

5  the present invention;

6

7  Figure 8 is a graph showing the current response to pre-

8  prepared brine solutions having different saturation

9  ratios; and

10

11  Figure 9 is a graph showing the correlation between the

12  saturation ratio for sample solutions and the slope of

13  the current similar to that of figure 8.

14

15  Figure 1 shows an electrochemical sensor setup comprising

16  an electrochemical cell rig 3, having the following

17  components. The electrochemical cell rig 3 comprises a

18  sensor (working electrode) 21 position proximate and

19  normal to the nozzle 9 through which a fluid jet (also

20  known as an impinging jet) exits from the nozzle 9. In

21  addition, the cell rig 18 provides support for a

22  reference electrode (silver-silver electrode) 19 and a

23  counting electrode 23 made of platinum, in this example.

24

25  The fluid control means consists of a pump 15 positioned

26  downstream of a needle valve 13 which is used to control

27  the flow level of the impinging jet fluid. A flow meter

28  7 is used to measure the amount of flow of the impinging

29  jet fluid so as to allow calculation of the Reynolds

30  number of the jet fluid. A nozzle 9 provides the means

31  by which the impinging jet fluid exits the fluid control

32  means 5 and contacts the working electrode 21. In this

1    example, a solution tank is provided for storage and

2    circulation of the impinging jet fluid.

3

4    Figure 2 is a graph of the limiting current $i_L$ measured

5    against the square root of Reynolds Number ($R_e^{\frac{1}{2}}$). The

6    graph 41 shows three curves. The first curve illustrates

7    a situation in which no scale has been deposited upon the

8    working electrode from the test fluid. Curve 45

9    illustrates the situation on an unscaled sensor. Curves

10   46, 47 and 48 illustrate the response from the sensor

11   with 22%, 39% and 46% of scale coverage respectively

12   after immersion for 1, 9 and 24 hours in a scaling

13   solution. These schematic representations show the

14   difference in the limiting current over the same range of

15   Reynolds number, where the level of scaling in the sample

16   is different.

17

| Immersion Time, Hrs | %Scale Coverage |
|---------------------|-----------------|
| 1                   | 22              |
| 9                   | 39              |
| 24                  | 46              |

18

19   Table 1 shows the resultant scale coverage for different

20   immersion times.

21

22   In use, the fluid control means or impinging jet system 5

23   is submerged in a fluid sample, and is used to control

24   the hydrodynamic regime at the surface of the working

25   electrode 21. Through analysis of the oxygen tracer

26   reduction reaction on the sensor surface, the extent of

27   scaling and the scaling tendency of the fluid can be

28   determined. In this example the test solution has a

29   saturation ratio of greater than 1 and is used to deposit

1   scale on the sensor surface.  A pre-prepared electrolyte

2   is used to determine the scale coverage.

3

4   The potential of the electrochemical sensor 1 is applied

5   to −0.8 volts (with respect to a silver/silver chloride

6   system) when measurements are started.  The impinging jet

7   system is then controlled through a range of Reynolds

8   numbers, and the limiting current response is measured as

9   a function of the Reynolds number.  Measuring the

10  relationship between these two variables, enables scaling

11  information to be obtained.  In this way, the amount of

12  scale and the scaling tendency of the test fluid can be

13  determined.

14

15  Figure 6 shows the limiting current correlation with

16  scaling index (log of saturation ratio) of the test fluid

17  (water containing electrolyte) for 6000s.  The

18  correlation between the scaling index and the

19  electrochemical measurement make it possible to measure

20  the scaling tendency of a fluid.

21

22  Figures 3 a to c and 4 provide more detailed explanation

23  of a sensor in accordance with the present invention.

24

25  Figure 3a is a graph 2 of limiting current versus

26  Reynolds Number$^{1/2}$ on a sensor.  Two curves 4 and 6

27  illustrate the change in limiting current as a function

28  of Reynolds number from initial values (curve 4) to final

29  values (curve 6).

30

31  Figure 3b shows the sensor surface 8 before the use of

32  the impinging jet which emanates from the nozzle, and

33  figure 3c shows the sensor surface after this operation.

1   The surface can be seen to be patchy as a result of scale

2   coverage.

3

4   Limiting current is given as follows:

$$I_{lim} = K \, Re^{1/2}$$

6

7   The a measure of the scale coverage on the sensor is

8   given by:

$$\text{Scale coverage} = (K_i - K_f)/K_i$$

10

11  Figure 4 shows the relationship between the nozzle 12

12  from which the impinging jet emanates and the sensor 22.

13  The nozzle has an inner diameter d 14 and the nozzle is

14  placed at a distance H 16 from the sensor 22.  Laminar

15  flow of the surface impinging jet occurs where:

16

17  $H/d = 1$; and

18  $r/d < 0.5$.

19

20  Figure 5 shows a second embodiment of the present

21  invention, in which the cell rig is installed in the

22  bypass system of a sub-sea pipeline.  The arrows 32 show

23  the direction of fluid flow through the system. The fluid

24  flow rate as quantified by calculation of the Reynolds

25  number is controlled through valves 37, 39 located in the

26  inlet and outlet of the bypass.

27

28  As shown in Figure 5, the bulk fluid 33 flows down

29  conduit 31 and a sample (the test fluid) of the bulk

30  fluid 33 is tapped from the bulk fluid conduit 31 to

31  measurement conduit or bypass system 35.  Once the test

32  fluid has been tapped, valves 37 and 39 are used to

33  control the fluid flow rate into the cell 3 where scale

1  is deposited on the working electrode 21. The working

2  electrode (sensor) 21 is connected to a potentiostat (not

3  shown)A flow meter (not shown) measures the flow rate. In

4  this example, to enable measurements of the extent of

5  scale to be made, the impinging jet is directed onto the

6  working electrode 21 and the fluid surrounding the sensor

7  is essentially static.

8

9  The output current from the electrochemical cell 3 over a

10  period of time enables the scaling tendency to be

11  measured.  Accordingly, the likelihood and speed with

12  which scale is likely to precipitate out from the bulk

13  fluid can be estimated.

14

15  The ability to operate the electrochemical sensor of the

16  present invention in situ allows the scaling tendency to

17  be monitored as the pressure, temperature, water

18  chemistry and other environmental conditions change.  By

19  locating the apparatus of the present invention within

20  the precise zone of interest within a pipeline, the

21  present invention can monitor the scaling tendency from

22  individual branches of a pipe in, for example, a

23  horizontal well which goes into the main pipeline.

24  Information feedback from the well can provide an early

25  indication of scaling potential problems.  Hence, the

26  present invention enables the operator to manage and

27  selectively control individual wells and to inject the

28  correct amount of scale inhibitor in these wells.

29

30  Further advantageously, the present invention can detect

31  small amounts of scale and can rapidly (within a matter

32  of 30 minutes or so) determine the scaling tendency of

33  the sample.  As a consequence, the operator of the

1   conduit, whether it be a riser from an oil well, a subsea

2   pipeline, a pipe in a desalination plant, or otherwise,

3   can quickly determine the scaling tendency in these

4   positions and can anticipate problems associated with the

5   build up of scale.

6

7   In use, the apparatus of the present invention will be

8   connected to an operator terminal by means of a suitable

9   telemetry system.  This will allow data to be collected

10  frequently by the operator using a communications

11  protocol.  Real-time data from the oil well or other

12  location will be sent to a PC based surface system that

13  monitors this location.  In addition, multiple systems

14  can be used at varying locations in a pipeline system or

15  well or the like, and all of these individual systems can

16  feed data back to a single PC for analysis by the

17  operator, who may then use this data to determine it is

18  necessary to add chemical scale inhibitors to that

19  location, or to otherwise remove or limit the scale

20  measured at that location.

21

22  Figure 7 shows a further embodiment of the present

23  invention similar to that shown in Figure 7.  Figure 7 is

24  an embodiment of the invention in which a pre-prepared

25  solution is used when measuring the scale coverage of a

26  working electrode.  The sensor arrangement 51 has two

27  fluid flow paths 53 and 55.

28

29  Flow path 53 is similar to the flow path shown in figure

30  7 and allows a fluid sample to be taken from a pipe 57

31  and fed through an electrochemical cell 61 via a conduit

32  59. Flow path 55 includes a solution tank 63 and a pump

33  69 which allow the supply of a pre-prepared electrolyte

1   (brine in this example) to the electrochemical cell rig.

2   It has been found that the use of this electrolyte allows

3   a more accurate measure of the scale coverage to be

4   achieved as the electrolyte is pre-prepared and

5   substantially free from the contaminants that are often

6   found in the bulk fluid contained in the pipeline 57.

7

8   A potentiostat 65 is used to measure the electrical

9   output of the electrochemical cell and this is connected

10  to a personal computer or network 69 by means of a

11  suitable connection.  This allows the end user to monitor

12  the scale coverage or scaling tendency from an office or

13  lab.

14

15  In order to measure scale coverage using this example of

16  the present invention, test fluid from the pipeline 57 is

17  fed into the electrochemical cell 61 via the conduit 59

18  and the control valve 58 such that the test fluid

19  continuously impinges upon the sensor surface 62. Valves

20  58 and 60 are used to control the rate at which the which

21  test fluid enters the cell, the flow is measured by a

22  flow meter (not shown) from which the Reynolds number can

23  be calculated. At this stage, the electrical output of

24  the cell 61 is not measured however, as the rate of test

25  fluid entry into the cell is a variable in the system, it

26  is desirable to control and measure this variable as it

27  shows the extent to which the flow is laminar or

28  turbulent. The test fluid flow is controlled so that it

29  continuously impinges upon the sensor surface 62 (working

30  electrode) for a predetermined period of time and scale

31  is deposited onto the sensor surface 62.

32

1   The extent of scale on the surface 62 is measured using

2   the pre-prepared electrolyte (typically an electrolytic

3   solution such as brine) and is provided to the cell 61

4   via flow path 55.  The brine solution is pumped

5   continuously through the cell 61 in a controlled manner

6   such that the Reynolds Number of the flowing brine can be

7   measured.  The scale coverage of the sensor 62 is

8   measured using the potentiostat 65 to record the output

9   current of the cell 61.

10

11  In this example of the present invention, the scaling

12  tendency of the test fluid is measured as follows. Test

13  fluid from the pipeline 57 is fed into the

14  electrochemical cell 61 via the conduit 59 and the

15  control valve 58 such that the test fluid continuously

16  impinges upon the sensor surface 62. Valves 58 and 60 are

17  used to control the rate at which the test fluid enters

18  the cell.  The Reynolds Number can therefore be

19  calculated.

20

21  The current output of the cell 61 is measured as a

22  function of time and the scaling tendency can be

23  calculated and provided to a user through the PC or

24  network 69.

25

26  Figure 8 is a graph 73 showing the current response

27  (current density) as a function of time for electrolytic

28  solutions (brine) having different saturation ratios.

29  The saturation ratios  for curves 75, 77, 79 and 81 are

30  17.8, 8.91, 0.27 and 1.09 respectively. Curve 79 has a

31  negative gradient.

32

1  Figure 9 is a graph 83 which illustrates the correlation
2  between saturation ratio and the slope of the current
3  values against time as exemplified in figure 8.
4  Curve 85 shows that scaling of the fluid does not occur
5  in region 89 where the saturation ratio is below
6  approximately 1 and scaling does occur in region 87 of
7  the graph 83 where the scaling ratio is above
8  approximately 1.  This region is where the fluid is
9  supersaturated.
10
11  The present invention has a number of advantages over the
12  known prior art.  In particular, the present invention
13  allows early measurement of scale or other particulates,
14  and provides a means by which the scaling tendency of the
15  fluid in question can be measured.  Measurement of the
16  scaling tendency, as well as the bulk amount of scale,
17  allows the operator to predict the amount of inhibitor
18  that should be used, and also to predict when in the
19  future this inhibitor should be applied.
20  Improvements and modifications may be incorporated
21  herein, without deviating from the scope of the
22  invention.